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(54) Title: LUBRICANT COMPOSITION BASED ON FISCHER-TROPSCH DERIVED BASE OILS

(57) Abstract: A lubricant composition having a dynamic viscosity at -35 °C of below 6200 cP as measured according to ASTM D 5293 and a mini rotary viscometer test value at -40 °C of below 60,000 cP as measured according to ASTM D 4684, comprising a Fischer-Tropsch derived base oil having a pour point from -15 to -31 °C and which base oil has been obtained by means of a catalytic dewaxing step, a pour point depressant additive 15 wt% or greater of a Detergent Inhibition (DI) additive package and Detergent Inhibitor (DI) additive package.

LUBRICANT COMPOSITION BASED ON FISCHER-TROPSCH DERIVED BASE OILS

Field of invention

5 The invention is directed to a lubricant composition comprising a Fischer-Tropsch derived base oils and one or more additives. The invention is especially directed to a lubricant composition according to the so-called SAE J300 classification.

Background of invention

10 Such lubricant compositions are also referred to as SAE xW-y compositions. SAE stands for Society of Automotive Engineers in the USA. The "x" number in such a designation is associated with a maximum viscosity requirement at low temperature for that composition as measured typically by a cold cranking simulator (VdCCS) under high shear. The second number "y" is associated
15 with a kinematic viscosity requirement at 100 °C as indicated below:

Engine Oil Viscosity Grade Specification (SEA J300)					
SAE Grade	Low temperature viscosities		High-temperature Viscosities		
	CCS Viscosity (cP)	MRV Viscosity (cP)	Kinematic viscosity at 100 °C (cSt)		HTHS Viscosity(cP)
	Max.	Max.	Min.	Max.	Min.
0 W (x)	6200 at -35 °C	60000 at -40 °C	3.8		
5 W	6600 at -30 °C	60000 at -35 °C	3.8		
10 W	7000 at -25 °C	60000 at -30 °C	4.1		
15 W	7000 at -20 °C	60000 at -25 °C	5.6		
20 W	9500 at -15 °C	60000 at -20 °C	5.6		
25 W	13000 at -10 °C	60000 at -15 °C	9.3		
20 (y)			5.6	<9.3	2.6 min
30			9.3	<12.5	2.9 min
40			12.5	<16.3	2.9 min 0W-40, 5W-40, 10W-30 grades
40			12.5	<16.3	3.7 min 15W-40, 20W-40, 25W-40, 40 grades
50			16.3	<21.9	3.7 min
60			21.9	<26.1	3.7 min

A lubricant composition comprising a Fischer-Tropsch derived base oils and one or more additives is for

example described in WO-A-0157166. This publication discloses a lubricant composition of 0W-20 and of the 0W-40 type consisting of a Fischer-Tropsch derived base oil. The pour points of the Fischer-Tropsch derived base 5 oils were respectively -66 °C (0W-20), -40 °C (0W-20), -66 °C (0W-40), -34 °C (0W-40), and -34 °C (0W-40) (between brackets are the lubricant type according to SAE J300 classification).

A disadvantage when blending the high tier lubricants 10 of the 0W-xx type as disclosed in WO-A-0157166 is that Fischer-Tropsch derived base oils are required which have a certain low pour point. Base oils having such low pour points may be obtained by for example a severe catalytic dewaxing process as disclosed in WO-A-0157166. A 15 disadvantage of such a process is that the lower the target pour point of the base oils the lower the yield to such base oils will be.

US-A-6103099 describes a 5W-30 passenger car motor oil formulation comprising a Fischer-Tropsch derived base 20 oil. The Fischer-Tropsch derived base oil was obtained by solvent dewaxing a partly isomerised Fischer-Tropsch wax. The base oil had a pour point of -18 °C.

US-A-6475960 describes in Example 2 a 15W-40 passenger car motor oil formulation comprising a Fischer-Tropsch derived base oil. The Fischer-Tropsch derived 25 base oil was obtained by solvent dewaxing a partly isomerised Fischer-Tropsch wax. The base oil had a pour point of -19 °C.

Showa Shell Sekiyu K.K. have sold since many years 30 a 5W-30 motor oil comprising a Fischer-Tropsch derived base oil. The Fischer-Tropsch derived XHVI type base oil is obtained by solvent dewaxing a partly isomerised Fischer-Tropsch wax. This partly isomerised wax is the SMDS Waxy Raffinate as prepared by Shell MDS Malaysia

Sdn Bhd. The XHVI type base oil has a pour point of about -18 °C.

EP-A-668342 describes a process to prepare a base oil from a partly isomerised Fischer-Tropsch wax, also referred to as waxy raffinate, by means of dewaxing said waxy raffinate. The dewaxing process could be solvent or catalytic dewaxing. The pour point of the base oil could be reduced by adding a pour point depressant additive. It is known that blending a 0W-xx motor oil can be achieved when using a severely hydrocracked and catalytically dewaxed mineral source base oil. But this is only when preparing formulations with a so-called Detergent Inhibitor (DI) package treats consistent with mainstream-tier finished lubricants, such as a GF-3 type formulation. DI packages in the context of the present invention comprise of a carrier fluid an anti-wear additive, an overbased detergent, an anti-oxidant and a detergent inhibitor. For package treats much above this level it has been found difficult to meet the cold-cranking requirements because of the combined base oil and package low temperature thickening effects.

If one wishes to extend performance levels to package treats consistent with top-tier performance, the severely hydrocracked mineral source base oils are less suited to obtain a 0W-xx motor oil.

Typically "mainstream" PCMO (Passenger Car Motor Oils) formulations contain about 10 wt% of a DI package, "premium tier" PCMO formulations contain about 12 wt% of the DI package and "top tier" PCMO formulations comprise of 15 wt% and higher of the DI package.

In order to obtain such a top-tier motor oil comprising the high package treat which is used in such products one will typically use a poly-alpha olefin type of base oil or a severely catalytically dewaxed Fischer-Tropsch derived base oil.

5 A disadvantage of the use of severely catalytic dewaxed base oil is that they are made by less selective processes as explained above. The use of poly-alpha olefins is less attractive because of their complicated process of preparation and higher cost. For example, the starting alpha olefins that are commercially used for this process are prepared by dehydrogenation of paraffins obtained in a Fischer-Tropsch reaction. It is thus much more attractive to prepare a base oil suitable for a high tier motor oil by means of a more direct and simple hydroprocessing of a Fischer-Tropsch wax itself.

10

15 The object of the present invention is to provide a high tier lubricant composition, which does not require Fischer-Tropsch base oil as prepared by a severe catalytic dewaxing process.

Summary of the invention.

20 This object is achieved with the following lubricant composition. A lubricant composition having a dynamic viscosity (VdCCS) at -35 °C of below 6200 cP as measured according to ASTM D 5293 and a mini rotary viscometer (MRV) test value at -40 °C of below 60,000 cP as measured according to ASTM D 4684, comprising a Fischer-Tropsch derived base oil having a pour point from -15 to -31 °C, a pour point depressant additive and 15 wt% or greater of a Detergent Inhibitor (DI) additive package.

25

Detailed description of the invention

30 Applicants found that it is possible to prepare a high-tier lubricant composition which complies to the 0W-xx requirements with a Fischer-Tropsch derived base oil which does not have such a low pour point as in the cited prior art publication.

35 The Fischer-Tropsch derived base oil has a pour point of point from -15 to -31 °C. The upper limit is preferably -20 °C. Pour points are measured according to ASTM D 97. The kinematic viscosity at 100 °C is

preferably greater than 3.5 cSt and more preferably between 3.5 and 6 cSt. Kinematic viscosity at 100 °C is as determined by ASTM D 445. The viscosity index (VI) is preferably greater than 120, more preferably greater than 130. The VI will typically be less than 160. Viscosity Index is as determined by ASTM D 2270. The Noack volatility (according to ASTM D 5800) is preferably less than 14 wt%.

5 The lubricant formulation comprises at least a pour point depressant additive. Preferably the amount of additive used is sufficient to provide the resulting lubricant composition the desired low temperature properties of the composition according to the invention. Applicants found a surprisingly high effect of the pour 10 point depressant additives in combination with the Fischer-Tropsch derived base oil allowing the use of a base oil having a pour point in the claimed range.

15 Suitable pour point depressant additives modify the wax crystal morphology such as to reduce interlocking of the wax crystals with consequent viscosity increase or gellation. Preferably as the pour point depressant alkylated naphthalene and phenolic polymers, 20 polymethacrylates, maleate/fumarate copolymer esters are used of which polymethacrylate, a methacrylate - vinyl pyrrolidone copolymer or a vinyl acetate - fumarate copolymer are preferred. Preferably at least 0.1 wt% of 25 such an additive is used. Preferably not more than 0.3 wt% of such an additive is used.

30 The lubricant composition will preferably also comprise one or more additives as for example described in the afore mentioned WO-A-0157166. Examples of additive types which may form part of the composition are viscosity modifiers, dispersants, detergents, extreme pressure/antiwear additives, antioxidants, pour point 35 depressants, emulsifiers, demulsifiers, corrosion

inhibitors, rust inhibitors, antistaining additives, friction modifiers. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, 5 pages 477-526.

Suitably the anti-wear additive is a zinc dialkyl dithiophosphate. Suitably the dispersant is an ashless dispersant, for example polybutylene succinimide polyamines or Mannic base type dispersants. Suitably the 10 detergent is an over-based metallic detergent, for example the phosphonate, sulfonate, phenolate or salicylate types as described in the above referred to General Textbook. Suitably the antioxidant is a hindered phenolic or aminic compound, for example alkylated or 15 styrenated diphenylamines or ionol derived hindered phenols. Examples of suitable antifoaming agents are polydimethylsiloxanes and polyethylene glycol ethers and esters.

The invention is directed to top tier PCMO 20 formulations having a Detergent Inhibitor (DI) package treat of 15 wt% and higher. Suitably the upper content of the DI package will be 20 wt%.

The DI Package or sometimes also referred to as Performance Package are commercially available from many 25 vendors and typically have the following composition: Dispersant additive between 40 and 50 wt%, Detergent additive between 15 and 20 wt%, Diluent Oil between 10 and 50 wt%, Anti wear additive between 8 and 12 wt%, 30 Ashless detergent additive between 5 and 15 wt% and Friction modifier additive between 1-2 wt%.

Next to the above package the Examples of DI additive packages a viscosity modifier additive may be present in an amount of between 0 and 20 wt% and a pour point depressant as describe above.

The Fischer-Tropsch derived base oil may be prepared according to the processes as disclosed in for example EP-A-776959, EP-A-668342, WO-A-9721788, WO-0015736, 5 WO-A-0014188, WO-A-0014187, WO-A-0014183, WO-A-0014179, WO-A-0008115, WO-A-9941332, EP-A-1029029, WO-A-0118156 and WO-A-0157166.

Preferably base oils are used which have been obtained in a catalytic pour point reducing process. The Fischer-Tropsch derived feed that is subjected to the 10 catalytic pour point reducing step may be obtained from every known Fischer-Tropsch synthesis process. Preferably a fraction of the Fischer-Tropsch synthesis product boiling substantially above 370 °C is used as dewaxer feed. Preferably part or all of the Fischer-Tropsch 15 synthesis product is first subjected to a hydrocracking/ hydroisomerisation step. In this step middle distillates are obtained. The residue as obtained as the bottom distillative product after such a hydrocracking step may be preferably used as feed to said catalytic pour 20 point reducing process. Examples of such processes are described in WO-A-02070631, WO-A-02070629 and WO-A-02070627.

Examples of catalytic treatments are for example the catalytic dewaxing or iso-dewaxing processes. The 25 catalytic pour point reducing processes comprise all processes wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a 30 metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base 35 oil precursor fraction under catalytic dewaxing

conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48.

5 Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other 10 molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Pt/ZSM-35, Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and 15 examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-4343692, US-A-5053373, US-A-5252527 and US-A-4574043.

20 A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate 25 zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. 30 Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and 35 EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, 5 preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. 10 By varying the temperature between 275, suitably between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having the desired pour points in a high yield.

15 From the effluent of the dewaxing step lower boiling non-base oil fractions are suitably first removed, preferably by means of distillation, optionally in combination with an initial flashing step. After removal of these lower boiling compounds the base oil having the 20 desired pour point and viscosity may be isolated, optionally after further distillation.

Examples

Various 0W-xx motor oil formulations were tried to be made starting from iso-viscous blends (at $V_k 100^\circ C$) or 25 single base oil iso-viscous($V_k 100^\circ C$) to said blends

- A. A base oil as prepared from a mineral source by means of severely hydrocracking and catalytically dewaxing
- B. A base oil as prepared from a mineral source by means of severely hydrocracking and catalytically dewaxing
- 30 C. A single base oil as prepared by severely catalytic dewaxing of a partly isomerised Fischer-Tropsch wax in accordance with the process as described in Example 1 of WO-A-02070629. The dewaxing severity was adjusted to arrive at the pour point of -30 °C for 35 the specified viscosity grade.

The above base oils were combined with a standard additive package, type passenger car motor oil, a pour point depressant and a viscosity modifier, type hydrogenated isoprene star polymer.

5 The results are in Table 1. In this table the following units are mentioned. The Kinematic viscosity at 100 °C (VK 100 °C) is determined by ASTM D 445, the Viscosity Index as determined by ASTM D 2270, the VDCCS @ -35 °C (P) stands for dynamic viscosity at -35 degrees Centigrade and is measured according to 10 ASTM D 5293, the MRV cP at -40 °C stands for mini rotary viscometer test and is measured according to ASTM D 4684, the pour point is according to ASTM D 97, and the Noack volatility is as determined by ASTM D 5800.

Table 1

Base Oils	Unit	0W-30 specifications	Base Oil A	Base oil (B)	Base Oil C
Kinematic viscosity at 100 °C	CSt		4.176	4.176	4.176
Viscosity Index	-		110	124	129
Pour Point		-18	-18	-30	
Motor Oil composition					
Base Oil	wt%		65.65	65.65	65.65
DI Additive package		15	15	15	15
Pour Point depressant additive		0.15	0.15	0.15	0.15
Viscosity Modifier additive		19.2	19.2	19.2	19.2
Blend Physicals 0W-30					
MRV at -40°C	CP	Less than 60000	43617	38809	21040

Viscosity at -35 °C	Less than 62	78.36	75.64	59.38
Kinematic viscosity at 100 °C	cSt Between 9.3-12.5	11.53	11.55	11.13

We further found that when a 0W-30 formulation is made using a solvent dewaxed Fischer-Tropsch base oil and a top-tier additive treat of 15 wt% it was not possible to meet the 0W-30 specifications because the MRV test 5 showed a yield stress and therefore the test was not passed.

Example 2

In Table 2 the blending properties of base oils D, E, F and G are compared.

10 D. A base oil as prepared from a mineral source by means of severely hydrocracking and catalytically dewaxing

E. A base oil as prepared from a mineral source by means of severely hydrocracking and catalytically dewaxing

F. A single base oil as prepared by severely catalytic dewaxing of a partly isomerised Fischer-Tropsch wax 15 in accordance with the process as described in Example 1 of WO-A-02070629. The dewaxing severity was adjusted to arrive at the pour point of -45 °C for the specified viscosity grade.

20 G. As Base Oil G but having a pour point of -43 °C.

Table 2 shows that with a the mineral oil based and a Fischer-Tropsch base oil it is possible to meet 0W-30 specifications with a lower DI additive package treat of 10 wt%. This is however not a top tier formulation 25 as defined elsewhere in this application.

Table 2

MRV at -40 °C	CP	Less than 60000	34100	36100	16400	19000
Vd CCS at -35 °C	P	Less than 62	67.90	64.40	42.97	56.23
Kinematic viscosity at 100 °C	cSt	Between 9.3-12.5	10.24	10.27	10.05	11.74
Noack	wt%		12.0	13.4	10.3	10.5

Table 2 shows that it is not possible to blend mainstream OW-30 formulation with mineral oil derived base oils.

Table 2 also shows that top tier OW-30 formulations can be blended using severely catalytically dewaxed Fischer-Tropsch base oils.

5

Example 3

10 The blending properties of Base Oil C was compared with Fischer-Tropsch base oils which were obtained by means of solvent dewaxing. These solvent dewaxed base oils are Base Oil H and Base oil I. To the base oils only 0.15 wt% of the pour point depressant additive of Example 1 was added.

The results show that only the catalytically dewaxed base oil C met the MRV requirements.

Table 3

Base Oils	Unit	Base Oil C	Base Oil (H)	Base Oil I
Kinematic viscosity at 100 °C	CSt	4.176	5.144	4.016
Viscosity Index	-	129	146	133
Pour Point	°C	-30	-15	-33
tested Oil composition				
Base Oil	wt%	99.85	99.85	99.85
DI Additive package	wt%	0	0	0
Pour Point depressant additive	wt%	0.15	0.15	0.15
Viscosity Modifier additive	wt%	0	0	0
MRV at -40 °C	cP	4950	Failed*	Failed*

* the MRV test showed a yield stress and therefore the test was not passed.

C L A I M S

1. A lubricant composition having a dynamic viscosity at -35 °C of below 6200 cP as measured according to ASTM D 5293 and a mini rotary viscometer test value at -40 °C of below 60,000 cP as measured according to 5 ASTM D 4684, comprising a Fischer-Tropsch derived base oil having a pour point from -15 to -31 °C and which base oil has been obtained by means of a catalytic dewaxing step, a pour point depressant additive and 15 wt% or greater of a Detergent Inhibition (DI) additive package.
- 10 2. Lubricant according to claim 1, wherein the content of a pour point depressant is greater than 0.1 wt%.
3. Lubricant according to claim 2, wherein the content of the pour point depressant additive is between 0.1 and 0.3 wt%.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M171/02 C10G65/04 C10M169/04
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10M C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01/34735 A (EXXONMOBIL RES & ENG CO) 17 May 2001 (2001-05-17) the whole document	1-3
Y	WO 02/070629 A (SHELL INTERNATIONALE RESERACH (NL)) 12 September 2002 (2002-09-12) cited in the application example 4	1-3
A	US 6 103 099 A (RYAN DANIEL F ET AL) 15 August 2000 (2000-08-15) cited in the application example 3; tables 3-9	1-3 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 475 960 B1 (HABEEB JACOB J ET AL) 5 November 2002 (2002-11-05) cited in the application claims 1,3,6; examples 1,8; tables 3,12	1-3
A	EP 0 668 342 A (SHELL INT RESEARCH) 23 August 1995 (1995-08-23) cited in the application page 7, lines 7-13 page 9, lines 48-53; claim 1	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

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